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Carbon Dioxide Corrosion and Acetate: A Hypothesis on the Influence of Microorganisms

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ABSTRACT

It is our hypothesis that fermentative, acetogenic, and sulfate-reducing bacteria residing in pipeline facilities can influence corrosion through the production of carbon dioxide and acetate under the prevailing anaerobic conditions. The exacerbation of carbon dioxide corrosion of carbon steel in the presence of acetic acid is a well-known phenomenon in the oil industry. Both chemical compounds can be produced and consumed by microorganisms during the anaerobic biodegradation of organic matter—including hydrocarbons. We contend that the principles governing anaerobic biodegradation activity can be extrapolated to aboveground oil production facilities and that the microbial diversity inherent in petroleum reservoirs largely reflects that in pipelines.

KEY WORDS: acetate, acetogenic bacteria, anaerobic biodegradation, carbon dioxide corrosion, fermentative bacteria, methanogens, microorganisms, sulfate-reducing bacteria

INTRODUCTION

It is generally agreed that carbon dioxide (CO_2) in oil pipelines originates from formation waters. CO_2 corrosion was first described in the 1940s,[1] and since that time much of the attention on CO_2 corrosion has focused on the resulting acidity when CO_2 is dissolved in water to form carbonic acid (H_2CO_3). Acetate is also recognized as a common constituent of reservoir fluids, and several hypotheses for the abiotic origin of this organic anion have been advanced. As summarized by Felipe, et al.,[2] these include the interaction of oil and water,[3-4] thermocatalytic degradation of kerogen,[5] oxidation of suitable acid precursors,[6-8] and the pyrolytic destruction of kerogen or oil components.[9-15] Simplistically, the corrosion rate of carbon steel in acetate-containing brines acidified by CO_2 is related to the concentration of acetic acid (CH_3COOH). Garsany, et al.,[16] using laboratory brines containing only sodium chloride (NaCl) and sodium acetate (CH_3COONa) concluded that the concentration of acetic acid is a function of the acetate concentration, and hence, there is a direct relationship between the corrosion rate of carbon steel and the acetate concentration of the brine. The distribution between acetic acid and acetate is a function of pH. The pKa of acetic acid/acetate in oil brines is near 4.7 (Figure 1).[16] In the bulk aqueous phase at normal pipeline pH values of ~6 to 6.5, a small fraction (~1%) of the acetate will persist as the protonated acid. However, in some locales associated with solids near pits, where a lower pH is observed, a considerably greater fraction may be protonated.

Crolet and Bonis[17] concluded that the key determinate of CO_2 corrosion was the chemical composition of the produced water and suggested that bicarbonate, acetate, hydrogen sulfide (H_2S), and calcium were as important for the evolution of pH as the partial pressure of CO_2. Crolet, et al.,[18] concluded that CO_2 corrosion was reduced at low partial pressures, unless

more than 0.1 mM to 1 mM acetic acid was present in the water. They concluded that one role of acetic acid in accelerating corrosion was related to an inversion of the acetate/bicarbonate ratio and that the acetic acid, even in a minute concentration, was the main source of the acidity consumed by corrosion.

The impact of "CO_2 corrosion" in oil and gas pipelines has recently been reviewed.[19] One of the conclusions of that article is that the electrochemistry of mild steel dissolution in CO_2 solutions is largely understood, but outstanding issues relating to the impact of other chemical components, in particular H_2S and acetic acid, still need a more fundamental understanding.

NACE Standard Practice SP0106-2006[20] specifies the following: (1) "A partial pressure of CO_2 above 207 kPa (30 psi) is usually corrosive in the presence of water. (2) A partial pressure of CO_2 between 21 kPa (3 psi) and 207 kPa (30 psi) may be corrosive in the presence of water. (3) A partial pressure of CO_2 below 21 kPa (3 psi) is generally considered noncorrosive." These specifications are followed with a cautionary note that low molecular weight organic acids (acetic and propionic) or H_2S will interfere.

Hedges and McVeigh summarized additional conclusions related to acetate in oilfield brines:[21]

—The presence of acetate ion in oilfield brines can significantly increase the rate of corrosion of carbon steel.

—In the presence of acetate ion, the corrosion rate can increase even if the pH increases. Many corrosion prediction models cannot accommodate this observation.

—On a ppm basis, acetate ion increases the corrosion rate more than HCO_3 decreases it.

—The presence of acetate ion only affects the corrosion rate and not the corrosion mechanism.

—The mechanism by which acetic acid increases the corrosion rate may be explained by its ability to both decrease the pH and solubilize Fe^{2+}, thus reducing the iron carbonate film thickness.

—Acetate ion has been shown to attack existing iron carbonate films and make them thinner. If local film thinning were to occur, this would result in localized corrosion.

—All of the above could result in the corrosion rate being significantly underestimated and consequently the specification of too low a corrosion allowance and/or the implementation of an insufficient inspection and corrosion control strategy.

Understanding the origin and fate of acetate in pipeline systems is fundamental for the appreciation of biologically mediated corrosion processes. Generally, a biological origin for acetate formation in reservoir fluids or in pipeline systems is not considered. Herein, we propose that both CO_2 and acetate pro-
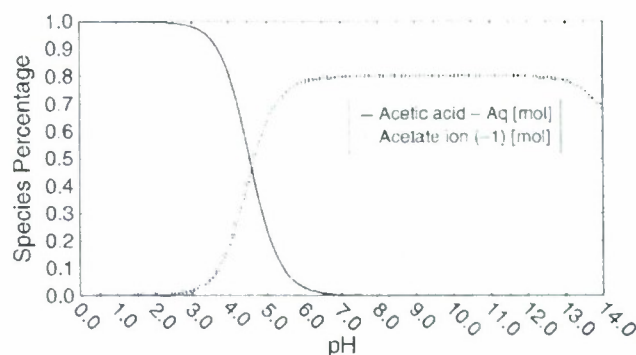

FIGURE 1. *Distribution of acetic acid and acetate based on pH.*

duced during the anaerobic biotransformation of organic matter in either the reservoir, in aboveground facilities, or both exacerbate the corrosion process.

EXTRAPOLATION OF ANAEROBIC BIODEGRADATION PRINCIPLES

Petroleum reservoirs harbor a diverse microflora.[22] Questions regarding whether such organisms are autochthonous inhabitants of such formations or allochthonous contaminants introduced during exploration are moot in that the microorganisms proliferate under the prevailing environmental conditions. It is therefore not unreasonable that some of these organisms get transported with reservoir fluids to occupy niches and exploit new habitats in pipelines, separation tanks, and storage facilities. Like the reservoirs, aboveground facilities are anaerobic environments and the metabolism of anaerobes, particularly those residing on or near metal surfaces, has the capacity to influence CO_2 corrosion in important ways.

Carbon Dioxide in Anaerobic Systems

First and most obviously, CO_2 is the ultimate mineralized end product resulting from the microbial degradation of the myriad forms of polysaccharides, proteins, nucleic acids, and lipids in any environment. Geological evidence suggests that hydrocarbons must be included in this list of biodegradable forms of organic matter.[23-24] In fact, the susceptibility of various hydrocarbons to anaerobic biodegradation is well known, and the subject has been reviewed repeatedly over the last decade.[25-36] It is clear that the oxidation of many different types of hydrocarbons can be coupled with the reduction of a variety of electron acceptors other than oxygen and that CO_2 is the resulting end product. It is also clear that anaerobes can couple their metabolism in syntrophic associations (below) that ultimately allow for the conversion of the petroleum components to the other major mineralized end product—methane (CH_4).[37-48]

As is typical in methanogenic environments, the catalytic entity involved is not a pure culture. This is

because methanogens are nutritionally limited and use only a few substrates, namely C1 compounds, hydrogen and acetate, to supply their carbon and energy needs. Methanogens must rely, therefore, on other anaerobes to convert complex forms of organic matter to simpler molecules that can then be assimilated. In effect, the methanogens, and in the presence of sulfate the sulfate reducers, may be the end members of a complex and rather modular feeding web wherein different organisms occupy specialized metabolic niches that serve to break down organic matter in a series of discrete stages.[49] However, the niche of methanogens is far more crucial than just scavenging small molecular weight metabolite fragments formed by partner organisms. In fact, the metabolism of larger molecular weight organic intermediates tends to be endergonic under standard conditions. That is, these compounds would not be readily metabolized unless the methanogens consume the aforementioned substrates and effectively pull the reactions toward complete mineralization. The net energetics of the coupled reactions are thermodynamically favorable. In this way, multiple organisms enter into thermodynamically based syntrophic associations with methanogens to affect the overall bioconversion of many forms of organic matter to methane and CO_2. The reactions continue to operate as long as the methanogens maintain the concentration of H_2 and acetate (formed at earlier metabolic steps) at low levels such that overall decomposition processes are exergonic. In syntrophic associations, the degradation of a substrate by one species is made thermodynamically possible through the removal of end products by another species. The mutual dependence between interacting bacteria can be so great that neither organism can function without its partner, and together the partners catalyze reactions that neither species can do alone. The intricate details of syntrophism with many examples of such interactions have recently been reviewed.[49-50]

We suggest that it is reasonable to expect the same type of mutualistic bacterial associations to also occur in facilities used for hydrocarbon extraction, processing, and transport. In these facilities, complex forms of organic matter including hydrocarbons are broken down into simpler components and eventually into smaller molecular weight fatty acids and alcohols. These components, in turn, are converted to acetate, hydrogen, and CO_2 by syntrophic bacteria that rely on the removal of acetate and hydrogen by methanogens (or other organisms—see below) to render the energetics of such bioconversions favorable. It should be clear from this brief discussion that many pathways of anaerobic metabolism converge on acetate. In effect, bacterial syntrophism can be based on interspecies acetate utilization as well as hydrogen consumption.[51-52]

The efficiency of methanogenic decay depends on the close cooperation between the partner organisms. There should be a balance between the decay of the primary substrate and the production of methane. Typically, intermediates like H_2 and acetate are maintained at suitably low concentrations.[49-50] However, there is no reason to expect that syntrophic partner organisms are equally sensitive to environmental stresses. Thus, the differential sensitivity to stresses can diminish and eventually destroy the mutualism between the organisms, and this most easily manifests itself as an accumulation of H_2 and acetate (as well as other reduced intermediates).

The situation changes in important ways if alternate electron acceptors (e.g., sulfate, ferric iron, nitrate, or several others) are present in sufficient amounts in anaerobic systems. In aboveground facilities the presence of sulfate from seawater injection systems and iron from metal surfaces are of particular concern. The anaerobic metabolism of organic matter can still occur under these conditions through the action of cooperating metabolic guilds of microorganisms. However, the composition of the guilds can change dramatically and methane tends to be far less quantitatively important an end product of microbial metabolism, particularly when sulfate is abundant. This is because organisms catalyzing anaerobic respiration at the expense of alternate electron acceptors are generally able to outcompete methanogenic consortia for critical metabolic intermediates like hydrogen and acetate.[53] The methanogens may also be directly inhibited in some cases. However, anaerobic respiratory metabolism in the presence of alternate electron acceptors can have a direct impact on corrosion through the production of reduced sulfides and direct iron dissolution.

ACETATE IN ANAEROBIC SYSTEMS

The reactions in Table 1 demonstrate the importance of acetate and H_2 as critical intermediates that are both produced and consumed in anaerobic environments under a variety of electron-accepting conditions. The role of acetate in accelerating CO_2 corrosion in pipelines would be particularly acute wherever the net production of this organic anion (from both biotic and abiotic sources) exceeds the ability of the end members of anaerobic microbial feeding webs to metabolize it. This would be particularly true where the acetate-consuming bacteria were inhibited or stressed relative to the acetate-producing organisms. In the simplest example, the methanogens tend to be very sensitive to pH and operate within a relatively narrow range. However, the same is not true of the other organisms that biodegrade higher molecular weight materials and produce acetate and other organic anions (as well as H_2 and CO_2). H_2 accumulation can also adversely affect methanogenic activity. Ahring, et al.,[56] found neither growth nor acetate utilization by the acetoclastic methanogen *Methanosarcina thermophila*

TABLE 1
Acetogenic, Methanogenic, and Sulfate-Reducing Reactions Involved
in the Degradation of Organic Matter Under Anaerobic Conditions[A]

Reaction		$\Delta G_0'$ [kJ/reaction]
Syntrophic acetogenic reactions		
$Propionate^- + 3H_2O$	$\longrightarrow$ $Acetate^- + HCO_3^- + H^+ + 3H_2$	76.1
$Butyrate^- + 2H_2O$	$\longrightarrow$ $2Acetate^- + H^+ + 2H_2$	48.3
$Lactate^- + 2H_2O$	$\longrightarrow$ $Acetate^- + HCO_3^- + H^+ + 2H_2$	−4.2
$Ethanol + H_2O$	$\longrightarrow$ $Acetate^- + H^+ + 2H_2$	9.6
$Methanol + 2H_2O$	$\longrightarrow$ $HCO_3^- + H^+ + 3H_2$	23.5
Methanogenic reactions		
$4H_2 + HCO_3 + H^+$	$\longrightarrow$ $CH_4 + 3H_2O$	−135.6
$Acetate^- + H_2O$	$\longrightarrow$ $CH_4 + HCO_3^-$	−31.0
$Methanol$	$\longrightarrow$ $3/4CH_4 + 1/4HCO_3^- + 1/4H^+ + 1/4H_2O$	−78.2
Sulfate-reducing reactions		
$4H_2 + SO_4^{2-} + H^+$	$\longrightarrow$ $HS^- + 4H_2O$	−151.9
$Acetate^- + SO_4^{2-}$	$\longrightarrow$ $2HCO_3^- + HS^-$	−47.6
$Propionate^- + 3/4SO_4^{2-}$	$\longrightarrow$ $Acetate^- + HCO_3^- + 3/4HS^- + 1/4H^+$	−37.7
$Butyrate^- + 1/2SO_4^{2-}$	$\longrightarrow$ $2Acetate^- + 1/2HS^- + 1/2H^+$	−27.8
$Lactate^- + 1/2SO_4^{2-}$	$\longrightarrow$ $Acetate^- + HCO_3^- + 1/2HS^- + 1/2H^+$	−80.0
$Ethanol + 1/2SO_4^{2-}$	$\longrightarrow$ $Acetate^- + 1/2HS^- + 1/2H^+ + H_2O$	−66.4
$Methanol + 3/4SO_4^{2-} + 1/4H^+$	$\longrightarrow$ $HCO_3^- + 3/4HS^-$	−90.4
Homoacetogenic reactions		
$Lactate^-$	$\longrightarrow$ $1 1/2Acetate^- + 1/2H^+$	−56.6
$Ethanol + HCO_3^-$	$\longrightarrow$ $1 1/2Acetate^- + H_2O + 1/2H^+$	−42.6
$Methanol + 1/2HCO_3^-$	$\longrightarrow$ $3/4Acetate^- + H_2O$	−55.0
$4H_2 + 2HCO_3^- + H^+$	$\longrightarrow$ $Acetate^- + 4H_2O$	−104.6

[A] Reprinted from Stams, et al.,[53] with the kind permission of Springer Science and Business Media. Some calculations have appeared elsewhere[54] and are based on the review of Thauer, et al.[55]

when H_2 levels were ≥1.99 μM. Similarly, a strain of *Methanosarcina barkeri* did not consume acetate until H_2 depletion occurred.[57]

As indicated above, we hypothesize that the microflora associated with oil production facilities largely reflects those found in petroleum reservoirs and that similar types of microbial associations can exist in both habitats. Three general groups of organisms responsible for acetate formation in anaerobic habitats are particularly noteworthy, but they are far from mutually exclusive. They are the fermenting bacteria, the acetogenic bacteria, and the sulfate-reducing bacteria. In consistent fashion, Magot[22] indicated that the major metabolic processes in oil reservoirs include sulfate reduction, methanogenesis, fermentation, and homoacetogenesis. While these may indeed be major processes, they do not preclude the existence of iron- and nitrate-reducing bacteria.[58] Organisms catalyzing these diverse metabolic processes can span a wide range of temperatures and salinity conditions.

Fermentative *Archaea* and *Bacteria* (see review by Ollivier and Cayol[58]) are anaerobes that use organic molecules as both electron donors and acceptors, and produce an array of end products whose identity is often characteristic of the organisms catalyzing the bioconversion. These organisms typically hydrolyze polymeric biomolecules like polysaccharides, proteins, and lipids. The same organism or others can con-

tinue to ferment the resulting sugars, peptides, amino acids, and longer-chain fatty acids. Typical products formed by these organisms not only include acetate as the most commonly produced end product, but longer-chain fatty acids, alcohols, formate, H_2, and CO_2. Many of the fermentative bacteria in oil reservoirs are capable of using inorganic sulfur compounds (S^0, thiosulfate), ferric iron, or nitrate as electron acceptors, although the latter is not commonly present in petroliferous environments.

End products produced during the fermentation of organic matter form the basis of many tightly coupled syntrophic interactions with other organisms in anaerobic environments. In fact, bacteria that syntrophically oxidize fatty acids were once believed to be strictly dependent on (e.g., H_2-, formate-, acetate-utilizing) partner organisms, since they could only be grown in co-cultures.[50] However, almost all known bacteria capable of syntrophic metabolism can now be grown fermentatively in pure culture with a more oxidized derivative of the parent substrate.

Another group of anaerobic bacteria capable for catalyzing the formation of acetate are the acetogens. Most of these organisms are able to grow at the expense of H_2 plus CO_2 as the sole energy source. They effectively compete for H_2 in anaerobic environments with other organisms and can easily constitute an end member of syntrophic partnerships. In effect, H_2

serves as the electron donor for CO_2 reduction to acetate in these organisms. There is precedence for the occurrence of acetogens in oil reservoirs but their presence and activity is only rarely determined. Acetogens were found to be the most numerically dominant cultivated organisms in a low-temperature and low-salinity petroleum reservoir,[59] and they have been reported in other types of petroleum formations as well.[60] Acetogens are not restricted to a lithotrophic lifestyle. Rather, these organisms are able to use very diverse electron donor and acceptor combinations and their in situ activities are not necessarily restricted to acetogenesis.[61-62] Since acetogens constitute a very phylogenetically and metabolically diverse bacteriological group, it is reasonable to anticipate that these organisms can inhabit and impact diverse habitats including oil pipelines.

The ability of bacteria to produce corrosive hydrogen sulfide from the reduction of sulfate, sulfite, thiosulfate, and elemental sulfur has been a chronic concern for the petroleum industry. These organisms are found in every anaerobic habitat examined to date and their population numbers are routinely monitored as part of pipeline integrity management efforts. They are an enormously diverse group of bacteria that can ferment both organic and inorganic compounds, use a wide variety of electron donors, and even reduce acceptors other than the aforementioned ones (for a recent review, see Muyzer and Stams[54]). In the absence of an electron acceptor, these organisms can enter into syntrophic relationships with methanogens or other H_2-consuming organisms. The ability to use carbohydrates tends to be rare. The diversity of sulfate-reducing prokaryotes found in oil reservoirs has been reviewed.[63] These organisms fall into two general groups—those that completely oxidize their organic substrates and produce CO_2 as an end product, and those that incompletely metabolize their substrates and produce acetate as well as CO_2. The complete oxidizers are able to utilize a wide variety of substrates including n-alkanes.[64-65] Thus far, hydrocarbon-degrading, incomplete-oxidizing, sulfate-reducing bacteria are not known. However, both types of sulfate-reducing bacteria have been isolated from oilfield production waters.[63] The ability of these organisms to both produce and consume acetate positions them as an important group of bacteria that may help regulate the concentration of this organic anion in pipeline systems.

POTENTIAL SIGNIFICANCE

Given the concerns over water, CO_2, and H_2S in carbon steel pipelines, fluids are typically dewatered and degassed to CO_2 partial pressures ranging from 0.1 bar to 0.3 bar (less than 5 psi of CO_2). However, even after degassing, anaerobic microbial metabolism can occur at the expense of numerous potential electron donors and acceptors. The requisite bacteria can catalyze such reactions as components of planktonic microbial assemblages or within biofilms developing on metal surfaces. As a result, we contend that CO_2 pipeline corrosion should no longer be considered strictly an abiotic process. The possibility of biotic in situ CO_2 as well as in situ acetate production has several important consequences. Measuring CO_2 at some initial point may not provide insight into the actual CO_2 content in a pipeline system. Further, there is no reason to expect that degassing incoming fluids to a desired level may effectively prevent CO_2 corrosion. Recognizing that in situ microbial CO_2 and acetate production may take place in bulk fluids or in localized areas of biofilm formation may ultimately allow for better pipeline integrity management assessments.

ACKNOWLEDGMENTS

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